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DIAMONDS

An untreated type Ib diamond exhibiting green transmission luminescence and H2 absorption. These contributors recently analyzed a small greenish brownish yellow ("olive yellow") diamond that exhibited green transmission luminescence (figure 1) as well as an unusual combination of absorption features. At first sight, the 0.12 ct diamond did not appear particularly remarkable, except for its UV luminescence, which was green to long-wave and greenish yellow to short-wave UV radiation. However, an infrared spectrum showed that the diamond was a low-nitrogen type Ib/IaA, with the single nitrogen clearly dominating the A-aggregates (figure 2; see specifically the inset showing the 1358–1000 cm^{-1} region). This was surprising, since green luminescence caused by the H3 center (the combination of paired nitrogen [A aggregate] with a vacancy) is commonly observed in type Ia diamonds but seen only very rarely in type Ib diamonds. Furthermore, the extremely low A aggregate concentration would not normally indicate the formation of distinct H3 luminescence. The total amount of nitrogen in the diamond was roughly

estimated from the spectrum to be 15 ppm by comparison with samples of known nitrogen content.

A strong "amber center" with its main peak at 4165 cm^{-1} was visible in the near-infrared region of the spectrum (again, see figure 2), indicating a deformation-related coloration. This also was unusual, since the amber center is typical for type Ia brown diamonds colored by deformation and related defects (L. DuPreez, "Paramagnetic Resonance and Optical Investigation of Defect Centres in Diamond," Ph.D. dissertation, University of Witwatersrand, Johannesburg, 1965). In "olive" and brown type Ib diamonds with deformation-related coloration, the main absorption of this defect has been found at 4115 cm^{-1} or as a doublet at 4165 and 4065 cm^{-1} (T. Hainschwang, "Classification and color origin of brown diamonds," Diplôme d'Université de Gemmologie, University of Nantes, France, 2003). A "single" amber-center peak at 4165 cm^{-1} in a type Ib diamond has not previously been described.

The deformation-related color was confirmed by observation in transmitted light between crossed polarizers. The diamond showed very distinct parallel gray to black extinc-



Figure 1. This 0.12 ct diamond, shown on the left in daylight, exhibits green transmission luminescence in dark-field illumination (right), as well as an unusual combination of absorption features. Photos by T. Hainschwang.

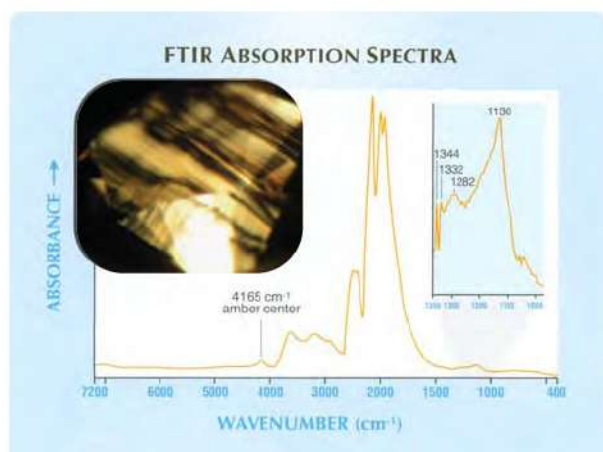


Figure 2. The FTIR spectrum of the diamond in figure 1 reveals that it is a type Ib/IaA, with isolated nitrogen clearly dominating the A-aggregates. The region between at least 5000 and 4165 cm^{-1} comprises the “amber center,” of which the 4165 cm^{-1} peak is the main feature. The amber center is deformation related; the deformation is apparent in the extinction patterns visible with crossed polarizers (see inset; photo by T. Hainschwang).

tion in two directions along octahedral growth planes, following “olive”-colored graining visible in the stone (figure 2, inset). This colored graining and extinction along the graining are very common features in “olive” diamonds. The order of extinction indicates that the stone is severely deformed and thus not optically isotropic. This is explained by the fact that the dislocations (broken bonds) caused by the deformation interfere with the direct passage of light that would be expected in truly isotropic materials. Even though strain associated with linear extinction and/or interference colors can be found to some degree in practically all diamonds, strong parallel extinction in a colored diamond provides a good indication for deformation-related coloration. Regardless of whether their green coloration is hydrogen- or radiation-related, “olive” diamonds seldom

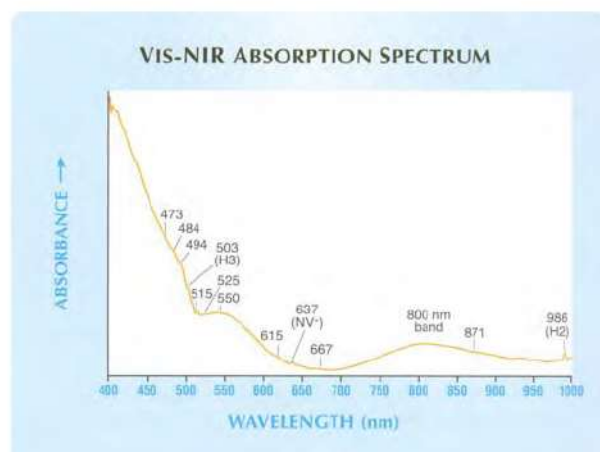


Figure 3. The low-temperature Vis-NIR spectrum of the diamond in figure 1 shows weak absorptions for the H3, NV⁻, and H2 centers, which is an unusual combination for an untreated natural diamond.

exhibit the strong strain pattern described here.

These observations prompted further analysis of the sample. A low-temperature spectrum was recorded in the visible/near-infrared range, which added to the unusual assemblage of absorption centers found in this diamond. The spectrum exhibited a combination of weak H3 (503 nm), NV⁻ (637 nm), and H2 (986 nm) absorptions with associated structures, plus moderate broad bands at about 550 and 800 nm (figure 3). The H3, NV⁻, and H2 absorption centers are typical of the visible-NIR spectra of HPHT-treated type Ia diamonds (A. T. Collins et al., “Colour changes produced in natural brown diamonds by high-pressure, high-temperature treatment,” *Diamond and Related Materials*, Vol. 9, 2000, pp. 113–122), and also can be created in type Ia or Ib diamonds through irradiation followed by annealing (A. M. Zaitsev, *Optical Properties of Diamond: A Data Handbook*, Springer-Verlag, Berlin, 2001, pp. 136–137), although these features typically are moderate to strong in treated-color diamonds.

Despite this correlation, other features indicated unambiguously that the diamond had not been treated by either method, and was indeed natural color. HPHT treatment of a brown-to-olive type Ib diamond, even at very moderate temperatures, would aggregate much of the single nitrogen and destroy the amber center (T. Hainschwang et al., “HPHT treatment of different classes of type I brown diamonds,” *Journal of Gemmology*, Vol. 29, 2004 [in press]; A. N. Katrusha et al., “Application of high-pressure high-temperature treatment to manipulate the defect-impurity content of natural diamond single crystals,” *Journal of Superhard Materials*, No. 3, 2004, pp. 47–54). Besides the temperature/pressure conditions, the aggregation is influenced by the total nitrogen content and the types of defects present. The combination of factors in

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this diamond would enhance nitrogen aggregation under commonly used HPHT conditions. In addition, irradiation of a type Ib diamond followed by annealing would create a very distinct NV⁻ absorption, resulting in pink to purple coloration (E. Bienemann-Küespert et al., *Gmelins Handbuch der Anorganischen Chemie*, Verlag Chemie, Weinheim, Germany, 1967, p. 237). Radiation treatment would also leave other traces, such as the 595 nm and the H1a and possibly H1b absorptions, which were not detected in this diamond.

The authors have recently seen the H2 center in a suite of very rare type Ib diamonds containing large concentrations of single-nitrogen that may exceed 400 ppm. These stones showed no deformation-related features and were distinctly different from the stone reported here. In contrast to these high-nitrogen type Ib diamonds, this is the first type Ib “H2 diamond” we have seen that shows a combination of H3, NV⁻, and H2 centers with classic strain patterns between crossed polarizers and a very low nitrogen concentration. The properties observed for this diamond are, at this point, difficult to explain. The deformation pattern and color distribution indicate octahedral growth and dynamic post-formation conditions. Besides the strong post-growth deformation and associated defects (dislocations, vacancies, and interstitials), the observed features suggest prolonged natural annealing at a low enough temperature to avoid aggregation of the single nitrogen, but nevertheless resulting in the combination of defects noted.

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